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PYROLYSIS OF POLYACRYLONITRILE AND RELATED POLYMERS—IV

THERMAL ANALYSIS OF POLYACRYLONITRILE IN THE PRESENCE OF ADDITIVES

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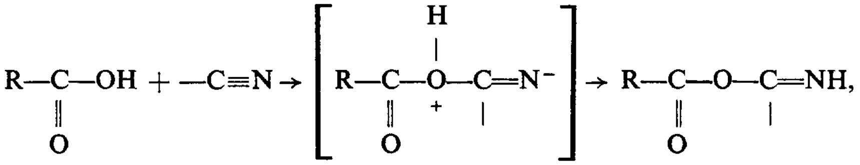
Abstract—The thermal behaviour of polyacrylonitrile studied by DTA and TG is shown to be greatly influenced by the presence of various types of additive. Pure PAN exhibits a very sharp exotherm at about 260°, caused by the oligomerization of nitrile groups. This reaction can be initiated at much lower temperatures by acidic and basic compounds and broad exotherms with much reduced differential temperatures are observed. Inorganic salts such as KCN, NaSCN and Na_2S also interact efficiently. An ionic mechanism is concluded for the additive catalysed reaction but, in the absence of additives, the reaction is shown to be free radical in nature.

INTRODUCTION

Previous studies(1,2) in this laboratory have shown that the colouration of nitrile polymers at low temperatures can be accelerated by certain additives. Carboxylic acids and phenols were found to be very reactive in the range 130–170°; strong inorganic bases induced colouration even at ambient temperatures. Certain amides, amines, ketones and alcohols were found to be rather less reactive. It was proposed that these compounds were capable of initiating the colouration reaction by nucleophilic attack on the nitrile group,



$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OH} + {-}\mathrm{C{\equiv}N} \rightarrow \left[\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{\underset{+}{O}}{-}\underset{|}{C}{=}N^-}\right] \rightarrow \mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}\underset{|}{C}{=}NH},$$

and that after initiation the reaction continued along the chain by a stepwise ionic mechanism to produce a ladder structure containing conjugated —C=N— sequences, the chromophore responsible for the colouration.

In more recent studies(3,4) of the pyrolysis of polyacrylonitrile by dynamic thermal analysis methods, it was found that colouration takes place very rapidly at higher temperatures (275 ± 25°); a sharp exotherm was observed by differential thermal analysis (DTA). It was concluded that both the exotherm and colouration were manifestations of the same reaction, namely the thermal polymerization of nitrile groups. It follows, therefore, that the DTA technique should be ideally suitable for detailed study of the effects of additives since changes in the nature of the exotherm will give much more rapid and accurate information than colouration experiments.

Another reason for the present study relates to the use of acrylonitrile polymers and

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copolymers in the manufacture of carbon fibre. In this respect the exothermicity of the pyrolysis is an undesirable feature which may cause excessive shrinkage, melting and disintegration of the fibres. The preferred process(5) therefore usually involves a low temperature isothermal treatment (pre-oxidation) to avoid the exothermicity of direct pyrolysis. In this study, the possibility of using additives to accelerate pre-oxidation, or indeed to remove the need for the step, is investigated. The effects of additives on the yield of carbon at high temperatures are also examined.

EXPERIMENTAL

Polymers

An acrylonitrile homopolymer (PAN) was used for most of the investigation; details of the preparation and properties of this polymer have been reported previously.(3) For comparison, a study was made of the commercial fibres, courtelle (Courtaulds Limited) and dralon (Bayer), both of which contain methyl acrylate as a comonomer.

Additives

It was found convenient to contaminate the polymer by rinsing with a solution of the additive. Weighed samples of PAN (20–50 mg) were placed in a sintered crucible and 2 ml of the additive solution added. Excess solution was pumped off and the polymer dried to constant weight. The solvent used depended on the additive but, where possible, a volatile solvent was selected to facilitate rapid removal of the solvent. It was found that solution concentrations of 1–5% gave 5–15% additive contents in the polymer.

Thermal analysis

A Du Pont Thermal Analyser incorporating differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TG) was used. For DTA and TG studies, the sample size was chosen such that it contained 10 mg PAN (i.e. sample size = 10 mg PAN + additive). The samples were pyrolysed at a heating rate of 10°/min in a dynamic nitrogen atmosphere. The sample size in the DSC experiments was 4–5 mg. Heats of reaction were calculated from the area of the DSC peak, the cell having been calibrated using the heats of fusion of pure metals.

RESULTS

Organic additives

DTA results obtained for PAN in the presence of additives, of types previously found(1) to be active initiators of the colouration reactions, are summarized in Table 1. Very large changes in the characteristics of the exotherm are obviously produced. Thus the exotherm is initiated at much lower temperatures and is spread out over a wide range. The maximum differential temperature varies but is much smaller than for pure PAN. When the additive concentration is very small, the low temperature initiation results in a tail or shoulder on the main reaction. As the additive concentration is increased, the exotherm becomes complex with several distinct maxima. Additive concentrations of 5–10% appear to be sufficient for maximum reduction of ΔT.

When these samples were examined by TG it was found that the weight loss curves were identical to that obtained from pure PAN. The reason is that, under the open sampling conditions in the TG analyser, the additive distils or sublimes out of the polymer before interaction can take place. This is illustrated in Fig. 1 which shows the DTA and TG curves for PAN/biphenol. The TG curve shows that the biphenol is removed below 180° and the PAN subsequently behaves as the pure polymer with an

TABLE 1. EFFECT OF COLOURATION INITIATORS ON THE DTA EXOTHERM OF PAN

Additive	Concentration (mg/10 mg PAN)	ΔT (C°)	T_S	T_R (°C)	T_I
None	—	34	298	264	245
Benzoic acid	1·0	3·4	265	262	170
Oxalic acid	1·5	4·7	237	232	210
		3·0	258	255	—
p-Toluic acid	2·0	2·0	230–250	—	195
m-Cresol	> 2·0	4·0	194	190	120
o-Methoxy phenol	> 2·0	6·0	202	196	115
		5·5	220	215	—
o,o' Biphenol	0·7	2·5	273	270	165
Succinimide	0·6	3·5	240	236	170
Urea	1·5	2·0	230	228	195
		3·0	268	265	—

Symbols: ΔT—maximum differential temperature.
T_S—sample temperature at ΔT.
T_R—reference temperature at peak ($T_R = T_S - \Delta T$).
T_I—approximate initiation temperature of the exotherm.

exothermic weight loss step at about 270°. In the DTA apparatus the sample is tightly packed and is shielded from the atmosphere by the ceramic sleeve of the thermocouple, so that the additive is less easily volatilized from the sample. It has been found that volatility under TG conditions is difficult to avoid with organic compounds. For example, *p*-chlorobenzoic acid, m.p. 241° sublimed from the polymer in the range 100–160°. Fatty acids up to stearic acid were also too volatile but a few di-acids, namely succinic, adipic and itaconic acids, did interact to a small extent and the exothermic weight loss step at 270° was reduced.

The most successful additives, with respect to interaction under TG conditions, are listed in Table 2. The weight losses have been corrected for the presence or loss of the

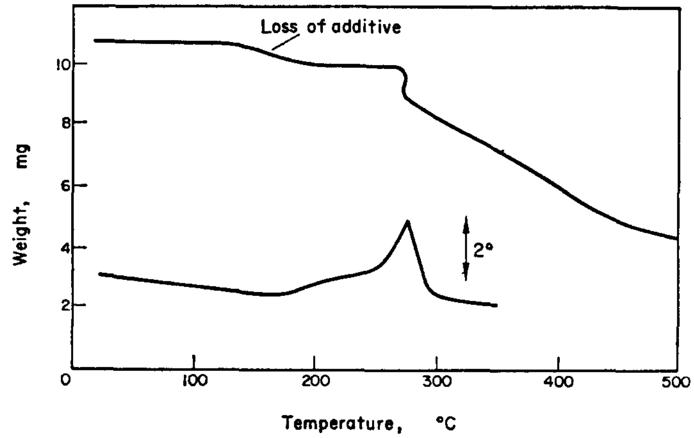


FIG. 1. DTA and TG curves for PAN-biphenol mixture. 10·7 mg sample heated at 10°/min under N_2 flow.

TABLE 2. ORGANIC ADDITIVES AFFECTING DTA AND TG BEHAVIOUR OF PAN

Additive	Concentration (mg/10 mg PAN)	ΔT (C°)	T_S (°C)	T_I (°C)	TG weight loss (%) 500°	TG weight loss (%) 1000°
None	—	34	298	245	56	72
Bisphenol A	0·7	0·7 2·0	186 250	155	14	61
Bisphenol A	0·2	3·5	259	165	18	60
Phloroglucinol	1·0	1·0 2·0	196 254	165 —	20	50
Sebacic acid	0·8	2·5 3·5	230 259	190 —	27	—
Gallic acid	1·5	4·0	230–245	200	40	—
Hippuric acid	1·0	4·0	273	205	20	58
Abietic acid	1·5	6·0	273	215	20	55
Tannic acid	0·9	5·0	263	200	20	52
Thiourea	0·6	2·0 2·5	231 285	200 —	29	—
Diphenyl guanidine	0·6	1·0 3·0	195 255	160 —	14	—
Guanidine acetate	0·6	2·5	226	175	14	56
Guanidine hydrochloride	0·7	5·0	268	200	16	62

additive and represent the weight losses for the polymer only. The Du Pont chart temperatures of 500° and 1000° correspond to true temperatures of 485° and 965°, respectively. The residue yield at 1000° is increased from 28% for pure PAN to 40–50% in the presence of these additives. The main difference is below 500°, however, where the weight loss is greatly reduced (see Fig. 2 in which the TG curves of PAN, PAN/phloroglucinol and PAN/Bisphenol A are compared).

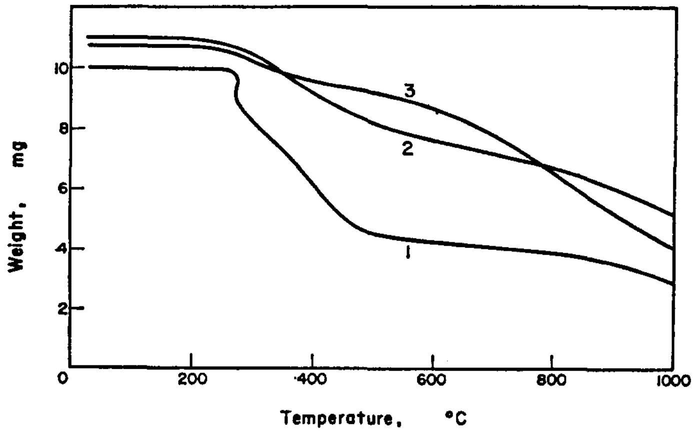


FIG. 2. TG curves for (1) PAN, (2) PAN-phloroglucinol and (3) PAN-bisphenol-A. Samples containing 10 mg PAN heated at 10°/min under N_2 flow.

TABLE 3. EFFECT OF INORGANIC ADDITIVES ON DTA AND TG OF PAN

Additive	Concentration (mg/10 mg PAN)	ΔT (C°)	T_S (°C)	T_i (°C)	Weight loss (%) 500°	Weight loss (%) 1000°
NaOH	1·0	1·0	140	100	19	74
		2·0	254	—		
Na_2S	1·0	5·0	250	170	28	—
NaSCN	0·8	6·5	300	240	30	56
NH_4SCN	1·4	3·0	222	195	*	
		2·0	270	—		
NH_4Cl	0·8	7·0	292	230	*	
$ZnCl_2$	0·8	0·8	225	170	30	60
		1·5	290			
$ZnCl_2$	0·2	2·6	295	170	16	62
KCN	0·7	1·8	248	175	26	57
H_2SO_4	1·0	6·0	282	200	16	55
H_3PO_4	1·6	5·0	292	240	16	60
H_3BO_3	0·5	6·0	365	340	45	—

* Additive volatilizes at low temperature.

Inorganic additives

The initiating ability of various types of inorganic compounds is demonstrated by the results in Table 3. Good interaction is again observed with both acidic and basic compounds. The Lewis acid, $ZnCl_2$, appears to be more efficient than the strong acids with respect to reducing ΔT. Various other types of salt including cyanides, thiocyanates and sulphides also interact. KCN appears to be particularly effective, producing small differential temperatures and good weight yields. The involatile nature of some of the inorganic additives results in the additive remaining as a contaminant throughout the pyrolysis treatment. This appears to have a deleterious effect on the carbon yield in the PAN/NaOH case which shows severe weight loss above 700°.

The anomalous behaviour of H_3BO_3 is interesting; although ΔT is reduced, the exotherm occurs at a much higher temperature than for pure PAN. The exotherm is fairly sharp and is preceded by a small endotherm as shown in Fig. 3(a). Weight loss is also retarded and is concurrent with the exotherm. It is concluded therefore, that H_3BO_3 acts as an inhibitor for the reaction rather than as an acid initiator. A free radical inhibitor, diphenyl picryl hydrazyl (DPPH), was studied for comparison; the results shown in Fig. 3(b) are very similar to those for boric acid.

Courtelle and dralon

DTA studies of courtelle and dralon in the presence of additives gave at first the surprising result that very little interaction was occurring between the additive and the polymer. This was due to the fact that these commercial fibres had received a surface finish which could act as a barrier to penetration of the additive into the fibre. The fibres were therefore washed with ether to remove the surface finish before doping with additives. The results obtained are given in Table 4. As previously found for PAN, the treated fibres show smaller differential temperatures although in the fibres the changes are less marked since the exotherms for the untreated fibres have much

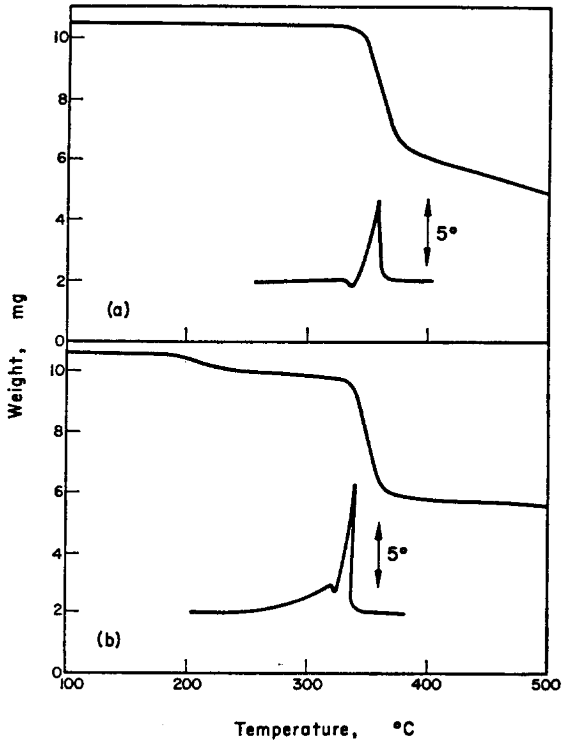


FIG. 3. DTA and TG curves for (a) PAN–H_3BO_3 and (b) PAN–DPPH. Samples containing 10 mg PAN heated at 10°/min under N_2 flow.

smaller ΔT values than PAN. The reason for this is that these fibres are equivalent to a PAN-additive system in that they contain small amounts of another monomer which is incorporated for dyeing purposes, but which also acts as an initiator of the exothermic reaction.

TABLE 4. EFFECT OF ADDITIVES ON THE DTA EXOTHERM OF COURTELLE (C) AND DRALON (D)

Fibre	Additive	Concentration (mg/10 mg fibre)	ΔT (C°)	T_s (°C)	T_i
C	None	—	7·0	290	215
C	NaOH	2·0	1·2	270	215
C	Benzoic acid	1·0	2·3	285	215
C	Tannic acid	1·0	4·2	270	215
D	None	—	7·0	294	245
D	NaOH	0·6	3·0	288	235
D	NaOH	2·0	1·5	255	195
D	Phloroglucinal	0·9	0·5 2·0	235–250 278	200 —
D	Hippuric acid	1·0	4·0	281	240
D	Gallic acid	1·0	3·0	270	225
D	Sebacic acid	0·6	3·0	275	240

DSC studies

The DTA study of PAN reported above shows that the shape of the exotherm is considerably changed by the presence of additives. It does not follow, however, that the total amount of heat liberated is altered. DSC results for selected samples are given in Table 5. The accuracy of these results is about ±10 per cent. The value of 7·4 kcal/mole found for the heat of reaction of pure PAN is a little higher than the value of 5–6 kcal/mole reported by Hay,(6) and slightly lower than the value of 8–11 kcal/mole reported for courtelle.(7) For some of the samples, ΔH is of the same order as the pure polymer but others show an increase in the heat of reaction.

Colouration and i.r. spectra

The development of colour during the inert pyrolysis of pure PAN is coincident with the exotherm and a tan-brown residue is obtained at 300°. Heat treatments to 275–300° in the presence of additives produced a range of yellow to brown residues. The changes in the i.r. spectrum of pure PAN heated to 300° have been discussed previously.(3) The main features are the reduction in the nitrile absorption at 2240 cm^{-1}, the appearance of a weak CN absorption at 2190 cm^{-1}, evidence for NH bonds in the range 3400–3200 cm^{-1} and very intense bands at 1620, 1580, 1300 and 1250 cm^{-1}. In the presence of additives, these changes are again observed and in some cases additional points of interest specific to the additive are found. Thus, PAN/carboxylic acid mixtures show a strong carbonyl absorption at about 1720 cm^{-1}, but at 275° this absorption disappears and the spectrum is identical to that obtained for pure PAN. Pyrolysis of PAN/NaOH and PAN/KCN produces a third CN absorption at about 2150 cm^{-1}. This is small in the NaOH case but fairly intense in the KCN sample in which the new absorption is much stronger than the residial CN at 2240 cm^{-1}. This new band is not present in the starting mixtures and is not caused by the metal cyanide; KCN absorbs at the lower frequency of 2075 cm^{-1}. It is concluded that an ionic nitrile species in the polymer is responsible for the absorption.

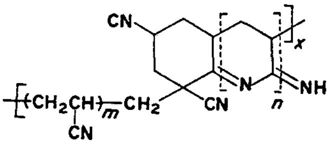
TABLE 5. HEATS OF REACTION OF PAN EXOTHERM

Additive	Concentration (mg/10 mg PAN)	$-\Delta H$ cal/g PAN	$-\Delta H$ kcal/mole CN
None	—	140 ± 10*	7·4
NaOH	0·5	143	7·6
KCN	0·7	121	6·4
$ZnCl_2$	1·4	159	8·4
Bisphenol A	0·7	137	7·2
Guanidine hydrochloride	0·7	176	9·3
Phloroglucinol	1·0	158	8·4
Sebacic acid	0·8	195	10·3
Tannic acid	0·9	183	9·7

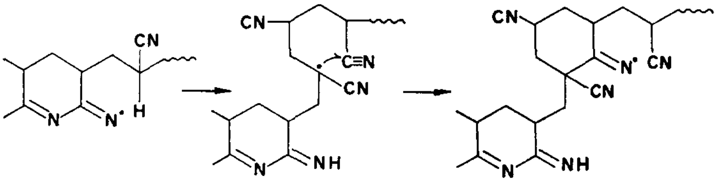
* Average value of several determinations.

DISCUSSION

The pyrolysis of pure PAN has been discussed at length previously.(3,4,8) The exothermicity results from the rearrangement of the nitrile groups to give cyclized structures. This corresponds to oligomerization of the nitrile groups and the structure of PAN heated through the exotherm can be represented by the general structure shown below:

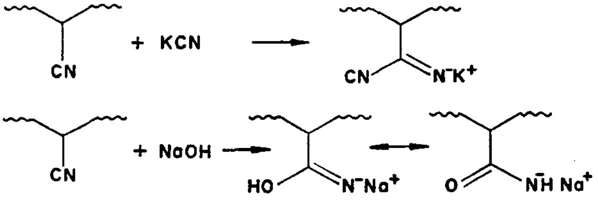


In this formula, m is considered to have values in the range 0–2; the most probable value is zero resulting in a structure consisting of cyclic segments linked by methylene bridges. The value of n is also small and the range 0–5 would appear reasonable. Formation of this imperfect ladder structure has been previously presented in terms of a free radical mechanism. Cyclization is initiated by active radicals resulting from the decomposition of defect structures in the polymer. Depending on the tacticity, propagating imino radials will attack the next nitrile group or abstract a hydrogen atom terminating that particular sequence. Cyclization is reinitiated as shown below:

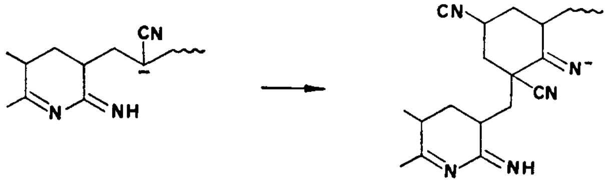


The structure of the pyrolysed polymer is modified further by elimination of HCN and NH_3 from the carbocyclic and imine end structures respectively. Chain scission also occurs especially during rapid pyrolysis so that a substantial weight fraction of chain fragments is formed. The free radical nature of these reactions, in the particular sample of polyacrylonitrile, is confirmed in the present work which showed that marked retardation of the exotherm can be obtained in the presence of free radical inhibitors. It is important to note, however, that a free radical mechanism is not always applicable. Thus the free radical inhibitor, DPPH, had no effect on the pyrolysis of another PAN which had been prepared by an anionic method. In anionic PAN, therefore, it appears that the degradation reactions proceed through ionic intermediates.

Most of the additives used in the present study have been found to be active initiators of the exothermic rearrangement reactions in PAN. In pure PAN, initiation appears to be the slow step and propagation is very rapid. In the presence of additives, the propagation reactions appear to be slower so that much broader exotherms are observed. This would be consistent with an ionic or concerted mechanism. With some of the inorganic initiators an ionic mechanism is easily visualized:

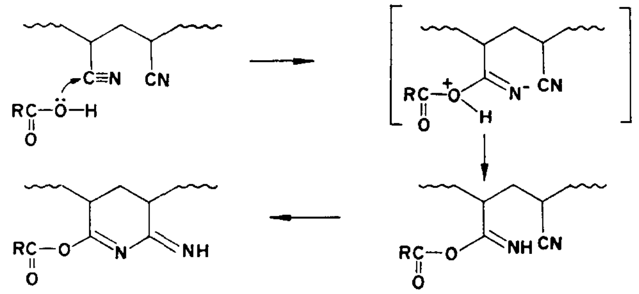


Slow propagation is explained by the fact that it would necessitate separation of the electrostatic charge or migration of the counter-ion. The i.r. spectra of PAN degraded in the presence of NaOH and KCN show a new nitrile absorption at about 2150 cm^{-1}. In pure PAN the appearance of a second nitrile absorption at 2190 cm^{-1} has been assigned to the iminonitrile structure corresponding to $n = 0$ in the general formula discussed above. The analogous ionic species could be responsible for the absorption at 2150 cm^{-1}. That is,

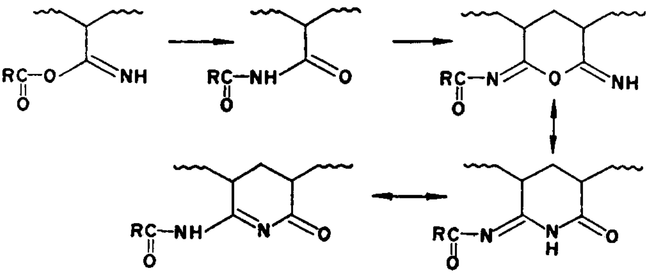


The 2150 cm^{-1} absorption is much more intense in the KCN sample than in the NaOH sample. As shown above however, direct initiation by KCN produces another ionic nitrile species, the α-iminonitrile ion; it is concluded that this species also absorbs at 2150 cm^{-1}.

Previous studies(1,2) of acid and phenol initiation indicated an ionic initiation mechanism followed by a concerted stepwise propagation:



Although the initiating ability of acids and phenols is beyond doubt, the mechanism shown here is not supported by the present study. In the structure above, the acid becomes an ester but the carbonyl group is not in conjugation with the ═C═N═ structure. Since the ester approximates to a vinyl ester, the carbonyl frequency should be higher than for the free acid and would be expected to be about 1750 cm^{-1}. PAN degraded in the presence of sebacic acid showed no absorption in this region. The complete disappearance of the carbonyl structure suggests that it has become part of the conjugated structure. A possible explanation is that the intermediate iminoester isomerizes to the imide form. This is the normal structure obtained from the reaction of acids and nitriles.(9)



Propagation via imide intermediates results, as illustrated, in conjugated structures in which the carbonyl groups may be in conjugation with the double bonds.

Irrespective of the nature of the propagating species, it is concluded that the structure of the degraded polymer does not change very much from that suggested for the purely thermal reaction. This is supported by the similar changes in colouration and i.r. spectra. It is also found that the total amount of heat liberated in additive initiated pyrolysis is not reduced. The fact that in some cases the heat of reaction is increased can be explained on the basis that the amount of heat observed is the net sum of the exothermic rearrangement and concurrent endothermic reactions, such as chain scission and the formation of HCN. TG studies show that the weight loss associated with the exotherm is reduced in the presence of initiating additives so that the endothermic contribution to the net ΔH is less. Much of the weight loss for pure PAN in the range 275–450° is caused by the distillation of chain fragments. The much larger amount of fragmentation obtained by vacuum pyrolysis as shown in Fig. 4(a) shows that much of the fragmentation occurs during the exotherm. In pyrolysis under nitrogen, the fragments are still formed but are large enough to be involatile at the temperature of formation. The good weight retention at 500° for PAN in the presence of additives suggests that the amount of fragmentation is reduced and this can be tested by vacuum pyrolysis. Figures 4(b) and 5 show the nitrogen and vacuum TG curves for PAN/tannic acid and PAN/KCN samples. The substantial weight loss

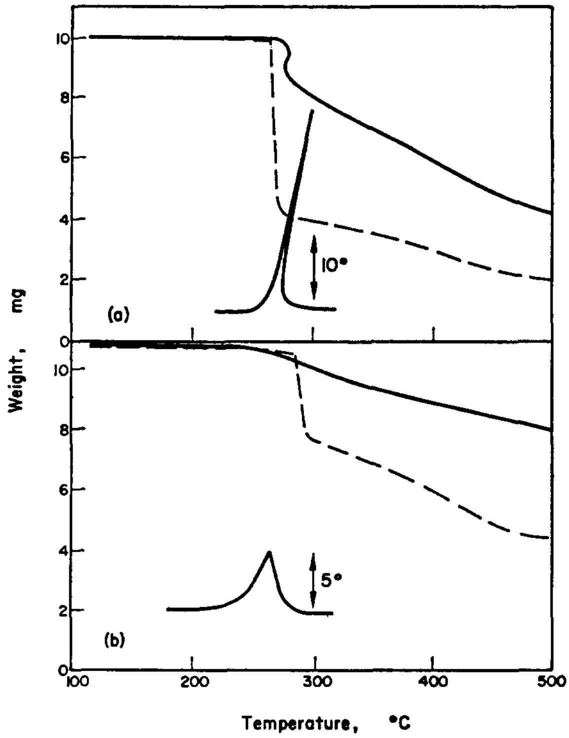


FIG. 4. Comparison of N_2 (——) and vacuum (– – –) TG curves of (a) PAN and (b) PAN-tannic acid. Samples containing 10 mg PAN heated at 10°/min. DTA curve included.

observed in the vacuum pyrolysis of the PAN–tannic acid sample demonstrates that fragmentation is still occurring but to a lesser extent than in pure PAN. The PAN–KCN case is more difficult to interpret. Thus, although fragmentation is not detected below 500°, the TG curves show increased weight loss in vacuum at higher temperatures. It is possible therefore that fragmentation did occur below 500° but, owing to the ionic species incorporated into the structure, the fragments are involatile below 500° irrespective of the TG atmosphere used.

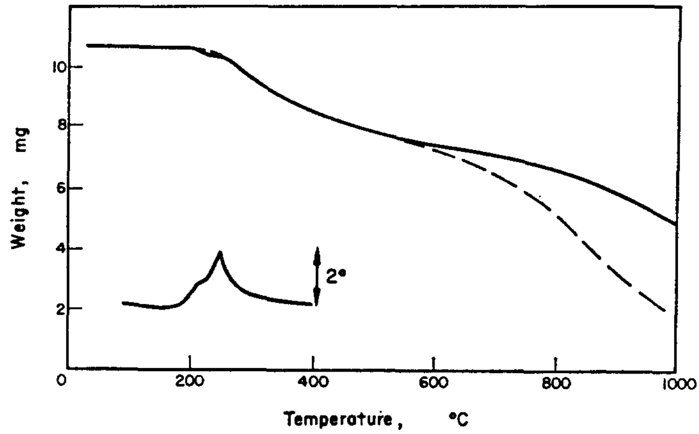


FIG. 5. TG curves in N_2 (——) and vacuum (- - -) of PAN–KCN. 10·7 mg sample heated at 10°/min. DTA curve included.

It is concluded therefore that, although the weight yield of carbon can be increased by pyrolysis in the presence of additives, fragmentation is not eliminated completely. Thus additive induced pyrolysis cannot be regarded as a substitute for pre-oxidation followed by pyrolysis; it has been shown previously[8] that an important function of pre-oxidation is to prevent fragmentation. Additives could be used however to accelerate the pre-oxidation treatment and reduce differential temperatures during the processing of carbon fibre.

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Résumé—On a montré par analyse thermique différentielle et par thermogravimétrie que le comportement thermique du polyacrylonitrile était foretement influencé par la présence de divers types d'additifs. Le PAN pur présente un pic exothermique très pointu à 260° environ, provoqué par l'oligomérisation des groupes nitriles. Cette réaction peut être amorcée à des températures beaucoup plus basses par des composés acides et basiques et on observe des pics exothermiques larges avec des températures différentielles plus réduites. Des sels minéraux tels que KCN, NaSCN et Na_2S réagissent aussi efficacement. Oh conclut que la réaction catalysée par un additif procède par un mécanisme ionique, mais, en l'absence d'additifs, on montre que cette réaction est de type radicalaire.

Sommario—Si mostra che il comportamento termico del poliacrilonitrile studiato mediante analisi DTA e TG, è notevolmente influenzato dalla presenza di vari tipi di additivi. Il poliacrilonitrile puro è molto esotermico a circa 260°, ciò che è causato dalla oligomerizzazione di gruppi nitrilici. Tale reazione può essere iniziata a temperature molto più basse mediante composti acidi e basici e si osservano comportamenti esotermici con temperature differenziali molto ridotte. Pure sali inorganici come KCN, NaSCN e Na_2S reagiscono reciprocamente in modo efficiente. Si conclude che per la reazione catalizzata dall'additivo entra in azione un meccanismo ionico però, in assenza di additivi, la reazione è di natura liberamente radicale.

Zusammenfassung—Das thermische Verhalten von Polyacrylnitril wird, wie aus DTA und TG Untersuchungen hervorgeht, stark beeinflußt durch die Gegenwart verschiedener Arten von Zusätzen. Reines PAN zeigt eine sehr scharfe Exotherme bei etwa 260°, hervorgerufen durch die Oligomerisierung von Nitrilgruppen. Diese Reaktion kann bei wesentlich tieferer Temperatur durch saure und basische Verbindungen ausgelöst werden, wobei man breite Exothermen beobachtet. Anorganische Salze wie KCN, NaSCN und Na_2S zeigen auch einen deutlichen Einfluß. Für die durch einen Zusatz katalysierte Reaktion wird ein ionischer Mechanismus angenommen, während gezeigt wird, daß die Reaktion bei Abwesenheit von Zusätzen über freie Radikale verläuft.